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Simultaneous Control of NOx and Organic Particles Using Plasma-Assisted Catalysis

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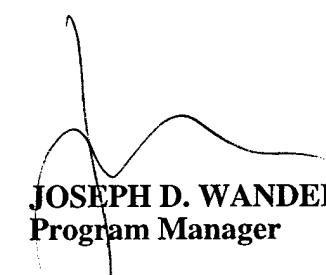
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13. ABSTRACT (Maximum 200 words) Water and higher concentrations of oxygen present in diesel and turbine combustion exhausts inhibit and deactivate selective reduction (SCR) catalysts that are effective in removing NOx from internal combustion engine exhausts. Oxidation of NO to NO ₂ , the slow step in SCR treatment, is accomplished rapidly as a competing process during plasma-catalyzed oxidation of hydrocarbon (HC) fuels in exhausts. Reduction of NO ₂ so formed is effected by passage of the heated stream through a bed of alumina of practically any configuration. Two-stage reactors to perform these steps were assembled and tested at bench-, pilot- and full-scale on exhaust from a 5.9-L Cummins diesel engine. The process, called plasma-assisted catalytic reduction (PACR), removed 95% of NOx at pilot scale using propene as the HC. Diesel fuel was used in the three sets of engine tests, and under these conditions PACR consistently achieved 50-55% reduction of NOx at a net fuel penalty of 5% to operate the control. Fuel sulfur did not affect the PACR process, and SO ₂ was not oxidized. Conduction across the high-voltage insulator was observed as a problem, but oxidation of deposited soot by the plasma was also observed and the system could be reconfigured using the plasma to prevent soot accumulation. Fuel cracking to enhance NO ₂ reduction was proposed but not tested.			
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Paper # 1055

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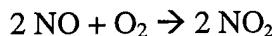
ABSTRACT

Current-generation diesel-powered equipment will not satisfy new-equipment standards for rates of NO_x emission scheduled to come into effect in 2004. SCR technologies being developed for the domestic market are dependent on the availability of low-sulfur fuels, which is not reliably available in deployed locations. An attractive alternative is Plasma-Assisted Catalytic Reduction (PACR), a two-stage process in which a nonthermal discharge (NTD) plasma induces oxidation of NO to NO₂ concurrent with direct oxidation of fuel hydrocarbons, and reaction at a catalytic surface immediately downstream reduces NO₂ to nitrogen. Feasibility of PACR has been demonstrated by a series of NTD experiments to characterize dependence of the redox processes on conditions, including the fuel supplied. Although kerosene hydrocarbons are less reactive than light alkenes, logistical requirements dictate that the same fuel that powers the engine be used in the PACR process. A working PACR model, which could be configured as a drop-in replacement for the muffler in the engine enclosure, was installed on a 5.9-L Cummins diesel engine and the engine-and-generator set was operated for 100 hours. In this test the 2004 NO_x standard was met at a net fuel cost of 5–6%. It is expected that incorporation of on-board capability to crack or reform the engine fuel to lighter hydrocarbons will decrease the net fuel cost. Soot-promoted arcing damage was detected, requiring the introduction of a soot filter immediately upstream of the PACR process. NTD induces oxidation of the carbonaceous residues collected on the filter surface, allowing regeneration of the filter in place.

INTRODUCTION

Practical combustion processes occur in inhomogeneous conditions, which promote formation of byproducts—soot in cool-burning, fuel-rich regions and NO in hot-burning, fuel-lean pockets—that are emitted in the engine exhaust as air pollutants. In addition, combustion is rarely complete, so partially oxidized and reformed byproducts—CO, aldehydes, benzene—are typically present in the exhaust as well. Hydrogenated members of the latter react in sunshine with NO₂ (which forms spontaneously from NO in air) to produce ozone in the low atmosphere and, because ozone and soot are recognized as pathogenic substances, incentives exist to decrease the rate of emission of pollutant byproducts from combustion-powered processes.

The term *Selective Catalytic Reduction* (SCR) encompasses a category of catalytic processes designed to reduce nitrogen oxides (NOx) to elemental nitrogen. In an idealized SCR process using ammonia as the reductant, two reactions occur:



and



The hazardous liabilities associated with ammonia can be avoided by substituting such derivatives as urea or cyanuric acid, but some reductant is needed to convert the oxygen present into water. The SCR reactions dominate over a relatively narrow range of temperatures. Conceivable process upsets may lower the temperature enough to allow emission (*slip*) of ammonia or raise it enough to cause oxidation of ammonia to produce additional NOx. And the catalysts are often expensive metals that interact with sulfur present in the fuels to suffer deactivation or to form sulfates, which eventually hydrate to form aerosols that have been implicated as health risks.

Low-sulfur fuels—synthetic hydrocarbons (HCs) and petroleum fraction that have been treated to remove most or all of the sulfur originally present—are coming on line as an enabling condition for practical introduction into mobile diesel engines of SCR technology based on HC reductants, under the designation *lean NOx catalysts*.¹⁻² Low-sulfur fuels play a critical role in the implementation of *lean NOx traps*³⁻⁴ and *catalytically regenerated particulate traps (CRT)*.⁵ In lean-NOx traps, the catalytic oxidation of NO to NO₂ on precious metals is followed by the formation of a nitrate on alkali or alkaline earth metal oxides. In CRT, a precious-metal catalyst is used to oxidize NO to NO₂ upstream of a particulate filter; the NO₂ is then utilized to oxidize the carbon fraction of the trapped particulates. The SCR, lean-NO_x trap and CRT technologies require low-sulfur fuel because the catalyst component that is active in converting NO into NO₂ is also active in converting SO₂ into SO₃. The SO₃ leads to the formation of sulfuric acid and sulfates that increase the particulates in the exhaust and/or poison the active sites on the catalyst.

Intense industrial activity is being directed at producing clean-burning personal and commercial vehicles using emissions control technologies that will rely on the availability of low-sulfur fuels. Whenever possible, the Department of Defense (DoD) acquires commercial products for all of its activities. However, low-sulfur fuels are a luxury that will normally not be supplied locally in theaters to which DoD forces are deployed. Thus any control technology that cannot tolerate extended operation with fuels of higher sulfur content than are currently used in the US may disqualify the equipment item using it for DoD operations. Additionally, the requirement for a reductant imposes a logistical requirement on any organization using or deploying the item to provide and handle the reductant.

Although reduction of NO and disproportionation back to the constituent elements are thermodynamically plausible processes, neither has been realized under real-world conditions. SCR invariably occurs as a two-step process, and the catalytically challenging step is the first one—NO appears to be resistant to almost all chemical advances (Figure 1). A notable exception is peroxy radicals, which occur as intermediates during HC oxidation, and which readily pass an

oxygen atom to NO. The Plasma-Assisted Catalytic Reduction (PACR) process⁶ evolves from this phenomenon. In the exhaust stream, a nonthermal discharge (NTD) plasma excites residual oxygen, which reinitiates combustion of HCs present. Reductants could be provided by adjusting the fuel-air ratio to the engine, but at present HCs are injected into the exhaust upstream of the NTD. NO parasitizes the radical combustion chain (Figure 2), undergoing oxidation to NO_2 as a consequence. The hydrocarbon-enhanced oxidation of NO to NO_2 in the plasma can be accomplished without oxidizing SO_2 to SO_3 .⁷ The effect is to sidestep the greater catalytic obstacle, leaving only the manageable task of reducing the NO_2 .

Figure 1. Temperature Dependence of Reactivities of NO and NO_2 Toward Propene Over γ -Alumina SCR Catalyst

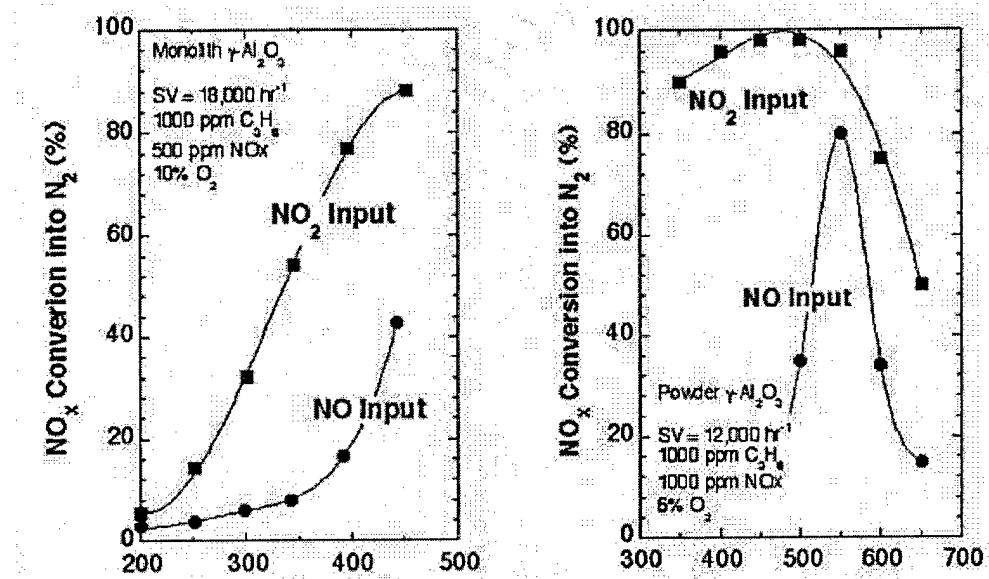
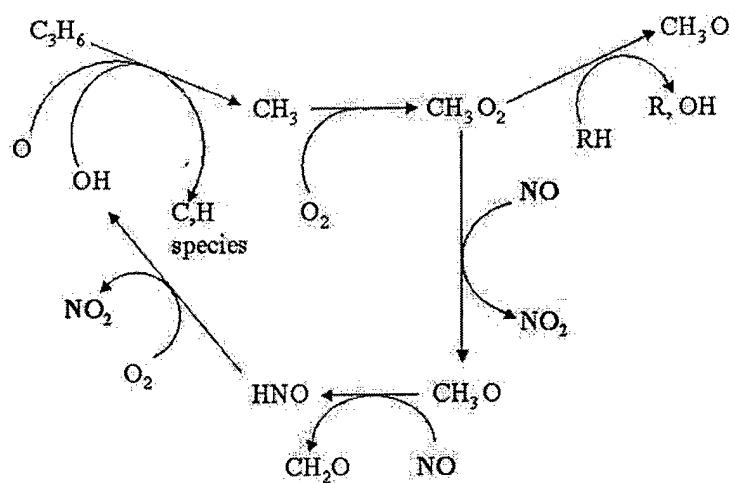
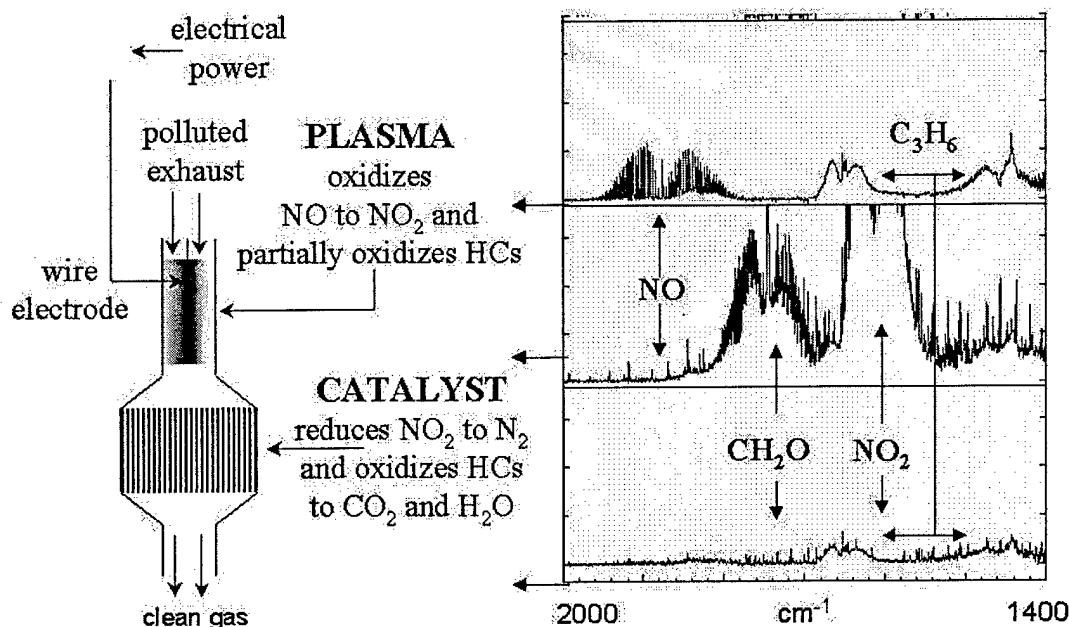


Figure 2. Example Chain Reaction Sequence for Propene Illustrating Concurrent Oxidation of NO.



At the start of this project LLNL researchers had assembled a bench-scale reactor system, comprising a sleeve-and-wire pulse corona discharge reactor connected to a bed of alumina beads (Figure 3). As drawn, the exhaust flows down through the plasma reactor and then through an alumina monolith. The chemistry of Figure 2 occurs in the plasma reactor, and NO₂ is reduced by residual HCs on the alumina surface.

Figure 3. Representation of PACR Process in Bench-Scale Sleeve-and-Wire NTD Plasma Reactor. FTIR Spectrum Illustrates Changes in Compositions Between Steps



Properties in the two regions are quite distinct. Reactions inside the plasma occur within a few milliseconds of excitation, so the space velocity in that region is effectively not a constraint in system design. In contrast, power consumption by the oxidation process decreases with increasing temperature when HCs are present to promote oxidation of NO. An exchange of power consumption for sensible heat would appear to be available, but requirements imposed by the catalytic stage limit this option. An energy density of 20 J/L was adopted as a practical working compromise. Power consumption is mass dependent, so the system design must include capacity to handle anticipated loads. Materials in excess of the capacity of the plasma pass through without reacting completely.

In the catalytic region, mass-transfer phenomena become important, whence reactivity depends strongly on contact time, limiting the rate that materials can be put through. The choice of catalysts is limited by the same considerations of hydrothermal deactivation, sulfur poisoning, and sulfate production that haunt the lean NO_x catalyst efforts; however, the requirement of the catalyst is significantly diminished by the presence of only NO₂ in the treatment stream.

An ongoing cooperative project between LLNL and Cummins Engine Co. (Columbus, Indiana) had set a minimum performance goal of 50% reduction of diesel engine tailpipe NO_x under

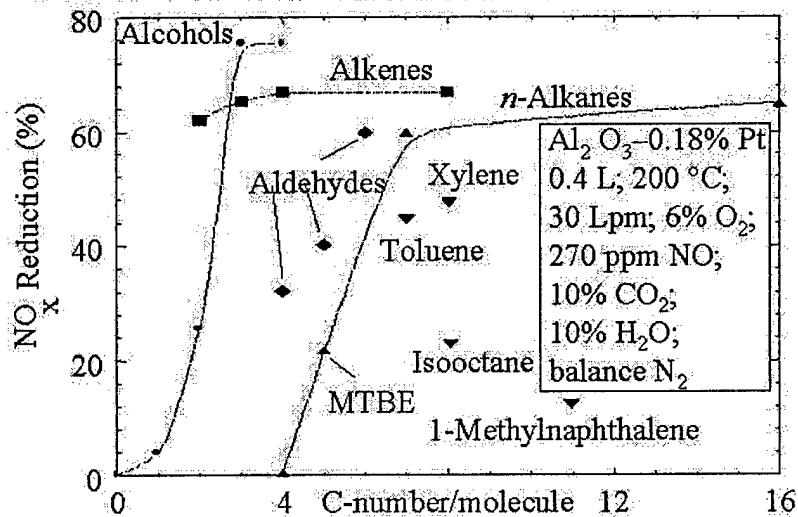
operating conditions that added no more than 5% to the engine's fuel consumption under the same productive load. For PACR this would include both the fuel HCs injected into the treatment process and power drawn off the generator to generate the plasma.

An inexpensive, rugged material— γ -alumina—proved effective as a monolith in the bench-scale study when propene was the HC reductant. Figure 1 shows that reduction of NO_2 by propene occurs at a fairly constant rate over a wide range of temperature. A number of other catalysts and configurations were tested during the course of this project, but none were more reactive than pellets of γ -alumina. Also favorable is the reported⁸ stability of γ -alumina catalysts under protracted exposure to diesel exhaust treatment conditions: Activity had decayed by only 20–30% after 4000 hours at 400 °C.

In the design of this study, the new boundary condition imposed on LLNL's ongoing effort was that the control device must function with the logistics fuel—typically DF- fuels or JP-8—that would be used to power the vehicle. Chemistry in the plasma is insensitive to sulfur content, but the reactivity of a mixture of primarily saturated liquid HCs ranging from C_9 – C_{15} is expected to differ from that of a pure, unsaturated HC gas.

The chemical class of the HC can be significant to deNOx performance.^{9–12} Saturates, such as methane, have been found to be generally weak deNOx reductants, while unsaturates, such as ethene and propene, have been found to be powerful deNOx reductants. Other studies have found both aliphatic unsaturates, typically alkenes, and aromatics to be associated with higher NOx conversions than with alkanes. The effect of the HC chain length on the deNOx activity has also been studied; long-chain alkane structures such as hexadecane have been observed to result in high conversions of NOx. A broad survey (Figure 4) of hydrocarbons having different chain lengths and functionalities under different but analogous conditions shows that, for a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst at 200 °C, the C_9 – C_{15} HCs in kerosene are half or less as reactive as C_3 – C_4 alkenes and alcohols on a per-pound basis.

Figure 4. Percent Reduction of NOx by Equimolar Amounts of Various Hydrocarbons (Relative to 800 ppm Propene).



PROGRESS

Subscale Pilot Studies

After a few additional experiments at bench scale, a modular, 200-Lpm engineering model of the PACR process was constructed on a laboratory rack. Accessibility and adaptability were principal considerations in the design and construction. The corona reactor was driven by a magnetic pulse compression power supply that delivers up to 30 kV output into 100-ns pulses at repetition rates up to kHz. A digital oscilloscope recorded both voltage and current profiles, which could be downloaded to a computer for long-term storage or analysis. Heated bands and thermocouples provided active control of the system temperature, from ambient temperature to 500 °C. A gas manifold was used to custom blend mixtures of six constituents: N₂, O₂, H₂O, CO₂, NO_x, and HCs as selected.

A Cummins 100-kW Genset powered by a modern 5.9-L diesel engine provided an exhaust stream for testing. The Genset was installed immediately outside the Laboratory, and a 200-Lpm split of the exhaust was piped through the wall into the experimental apparatus. The exhaust manifold of the engine was modified by the insertion of a stainless steel line through which HCs were delivered into the hot exhaust stream. A flame ionization detector (FID) was used to monitor HC concentration in the exhaust stream. A chemiluminescence NO_x analyzer and a Fourier-transform infrared (FTIR) spectrometer were used to monitor gas composition. To prevent condensation of water in the exhaust gases, the 6-m White cell in the FTIR was maintained at 120 °C.

When heaters, seals and couplings had been properly adjusted, initial runs of the pilot unit confirmed that the HCs in DF-2 (diesel fuel) were less than half as reactive as propene under the conditions used at bench scale. Efficiency of mixing is always a concern in combustion systems, and the substitution of a liquid fuel for a gas would be sensitive to imperfect mixing conditions. No method was available for directly interrogating the mixing phenomena, so a second line to permit injection of fuel was inserted into the test apparatus, slightly upstream of the plasma reactor. The fuel at the second point was wicked into a heated chamber to effect evaporation before delivery into the exhaust stream slightly upstream of the plasma. A series of runs comparing performance using the two injection methods showed that they were equivalent. From this it was concluded that mixing was efficient under both conditions. A second benefit of injecting HCs inside the test system is that the rate of HC delivery is 2% that required to treat the entire flow before the split, and the inside injector was used throughout the remainder of the pilot study.

When it had been established that intrinsic reactivity of DF-2 (and presumably any other kerosene) is significantly less than that of propene, the effect was investigated. Figure 5 shows that both diesel fuel and kerosene are as reactive at low concentrations in the plasma as propene, and that they are slightly more reactive at higher concentrations. Figure 6 shows that propene is more reactive at intermediate concentrations, and that the liquids catch up at higher concentrations. At 20 J/L, power consumption by the plasma accounts for approximately half the

fuel penalty allowed, so the concentration attainable is limited. A separate set of experiments determined that SO_2 is not oxidized to SO_3 during either step of the PACR process.⁷

Figure 5. Efficiency of Plasma-Catalyzed NO Oxidation at 300 °C by Three Different Fuels.

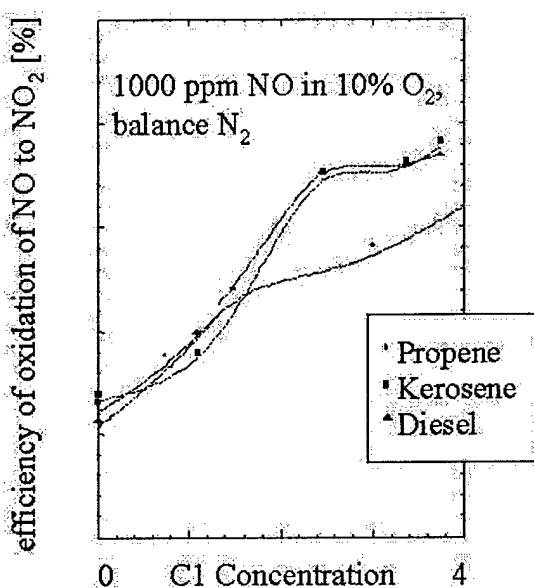
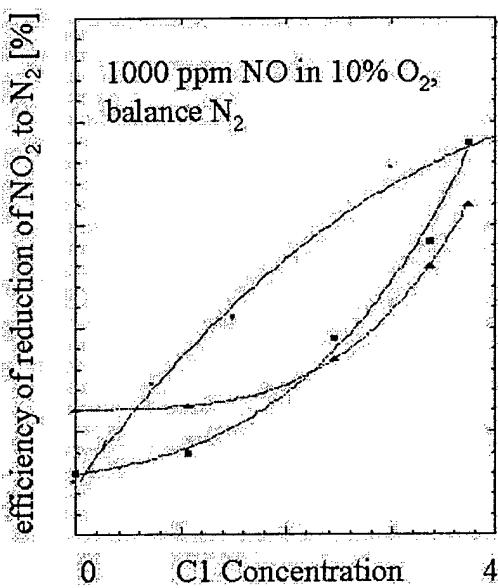


Figure 6. Efficiency of Reduction of NO_2 over Alumina at 300 °C by Three Different Fuels.



Whereas a survey of alternative catalysts produced no better candidate than alumina, the PACR system met the standard of 50% reduction (satisfying the 2004 emission limits) at 5% fuel penalty (satisfying DOE's criterion). Thus the effort continued to a full-scale demonstration.

Full-Scale Pilot Studies

Scalability and reliability were the principal questions to be addressed in the full-scale exercise, as the chemistry held constant between bench and subscale pilot tests. All components of the system were fabricated from scratch, and component shakedown tests and adjustments followed by a system shakedown and adjustments consumed the first few months. A ceramic sleeve was inserted inside the cylindrical outer electrode, converting the mode of plasma generation to barrier discharge. This decreased demands on the power supply, which would otherwise have been prohibitively expensive to assemble. After preliminary testing and tuning in the lab, the full-scale PACR unit was carried outside mounted in an angle-iron frame and installed on the exhaust of the Genset. Insulation and thermocouple-controlled heaters maintained positive thermal control. The same analytical systems were employed to monitor concentrations.

Concurrent with fabrication and adjustment of the plasma electronics and reactor, different configurations of catalysts were studied. In particular a series of tests compared performance of a wash coat applied to alumina pellets and the same wash coat on an alumina monolith in which alternating channels were plugged at opposite ends, which forces flow to permeate through the

walls. The result of the tests was that the configuration did not affect the efficiency of conversion. This excluded the possibility of mass-transfer control of the process, and indicated that the process operates under kinetic control. A developmental zeolite catalyst submitted by a manufacturer showed twice the activity of alumina in preliminary tests at 200 °C, but experienced rapid deactivation at 5% concentrations of water. Water content of the Genset exhaust was determined to increase linearly from 2% near zero load to 8% at full load. The zeolite was dismissed as incompatible with operating conditions, and pelletized alumina remained the catalyst of choice.

After a brief period of system checks the Genset and control were operated as a unit in 5-hour shifts for four working weeks. As during the pilot tests, NOx removal under normal operating conditions ranged from 50–55%. Fuel consumption was nearly 6%, so a claim of success requires slight qualification.

Operation throughout the test period was uneventful, and a teardown and analysis was expected to be routine. However, the flange through which the high-voltage lead to the center electrode passes had accumulated a coating of soot that attracted an arc from the high-voltage pulses. The eroded crack had penetrated halfway through the flange at the time of the teardown (100 hours in service), and failure was imminent. The ceramic sleeve inside the reactor displayed soot only outside the region of plasma generation.

A substantial redesign of the system was required before a companion set of tests could be run as a retrofit to an older generator set, the A/M-32A-86. Initial tests after the –86 unit arrived from McClellan AFB revealed that operating temperatures of the two-cycle engine, which is chronically operated at about 2–3% of rated capacity, are much lower than the operating range of the Cummins engine, and that liquid HCs accumulate inside the exhaust system. An incidental benefit to drawing power to operate the control for the –86 is that the increased load will raise the engine temperature and improve the overall performance of the unit in its usual mode of use.

Thus it was necessary to redesign the PACR unit to isolate the plasma processor from the brunt of the soot in the exhaust, and for the –86 test it had also to oxidize accumulated fuel. The clean area of the ceramic sleeve points up that the plasma can oxidize soot accumulated on surfaces, and this technology has been proposed as a means of removing soot from diesel exhaust filters. A bag filter membrane was mounted (Figure 7, left) in an exhaust stream, loaded, and exposed to a plasma. The shape of the electrodes (Figure 7, right) can be discriminated in the area cleaned by the application of plasma, demonstrating the feasibility of using the plasma to clean soot on filter surfaces. Analysis of the exhaust stream produced during this cleaning operation (Figure 8) revealed virtually complete oxidation, but concurrent formation of NO₂, which a catalyst downstream might eliminate.

A tool to guide the redesign process is a map of contours describing efficiency of oxidation of NO by the plasma under varying conditions of fuel-to-NOx ratio and applied plasma power (Figure 9). Another option discussed but not yet investigated is to introduce a cracking or reforming catalyst that would be thermally coupled to the exhaust manifold and activated by engine heat. Such a notion follows from the concept of endothermic fuel conversions as a cooling mechanism for hypersonic aircraft, but catalyst selection for this will likely be no less a

challenge than securing a better catalyst for reducing NO in the second stage of the PACR process.

Figure 7. Removal of Soot from Filter Surface by Local Application of a Nonthermal Plasma. The Configuration of the Electrodes is Sketched at the Right.

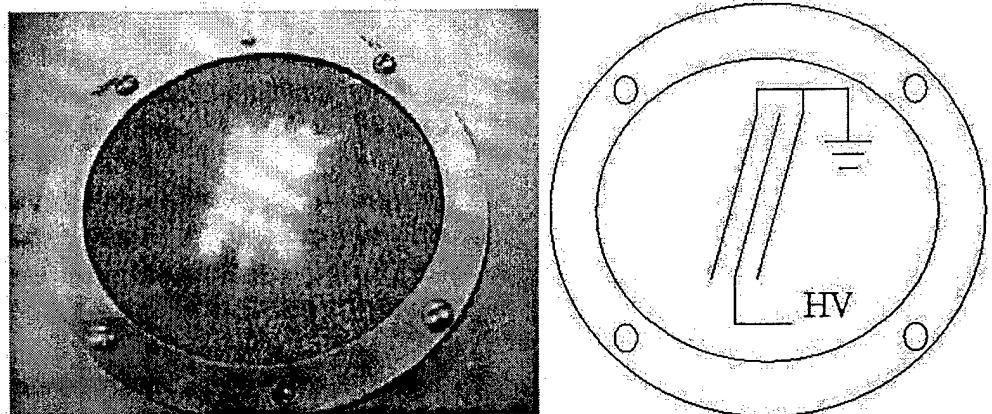


Figure 8. FTIR spectrum of Exhaust Gases from Plasma-Catalyzed Regeneration of the Soot Filter Depicted in Figure 7.

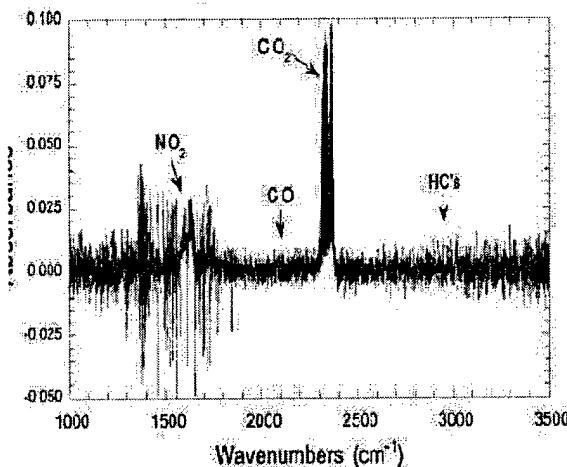
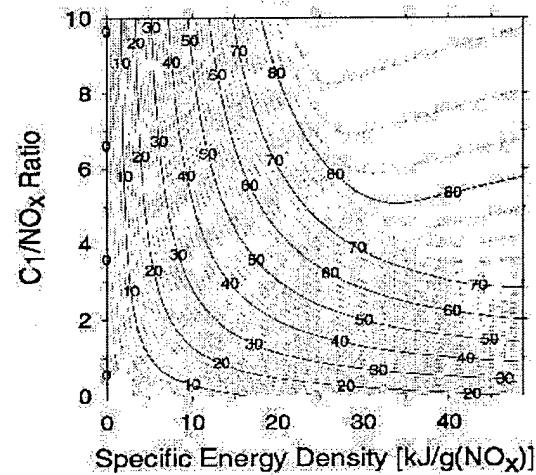


Figure 9. Constant-Conversion Surfaces for Fuel/NO_x Ratio and Power Applied: Plasma NO-to-NO₂ Oxidation Efficiency



SUMMARY

Results to date suggest that, with further development, the PACR process may be able to compete effectively as a control technology for NO_x and soot. The future for military applications may be even brighter if mobility requirements disqualify the set of technologies ultimately selected by DoD's commercial suppliers to achieve future emission standards.

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KEYWORDS

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